CATALYTIC WET AIR OXIDATION OF WASTEWATER CONTAINING ACETIC ACID

by

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LIST OF ABBREVIATIONS

BET	Brunauer, Emmett and Teller
CWAO	Catalytic Wet Air Oxidation
GC	Gas Chromatography
TOC	Total Organic Carbon
WAO	Wet Air Oxidation
XRD	X–ray Diffraction

PEMANGKIN PENGOKSIDAAN UDARA BASAH AIR SISA MENGANDUNGI ASID ASETIK

ABSTRAK

Air sisa mengandungi asid asetik telah lama dihasilkan oleh industri kimia. Pelupusan sisa ini yang tidak betul telah menjadi masalah yang besar kerana sisa tersebut mencemarkan alam sekitar dan memusnahkan ekosistem akua. Air sisa ini harus dirawat sebelum dilepaskan kea lam sekitar. Antara kaedah rawatan termasuk penggunaan membran dan pengoksidaan udara basah. Kaedah ini mempunyai beberapa batasan. Proses membran terhad oleh kestabilan pelarut dan kestabilan terma dan pengoksidaan udara basah hanya berkesan pada keadaan operasi yang tinggi. Dalam kajian ini, pemangkin pengoksidaan udara basah adalah kaedah yang dicadangkan untuk rawatan. Pemangkin telah disintesis berdasarkan kepada kaedah kebasahan. Eksperimen telah dijalankan dengan mengoksidakan air kumbahan simulasi mengandungi asid asetik dalam reaktor berkelompok. Kajian tindak balas diulangi dengan manipulasi dua operasi parameter yang berbeza. Sampel telah dianalisis menggunakan analisis Jumlah Karbon Organik dan Kromatografi Gas. Pemangkin dicirikan oleh analisis Pembelauan Sinar X dan analisis *Physisorption (BET Method)*. Pemangkin pengoksidaan udara basah menghasilkan penukaran tertinggi pada suhu 80°C. Pemangkin yang mempunyai kawasan permukaan tinggi telah disahkan oleh analisis Pembelauan Sinar X dan *Physisorption*. Penukaran menggunakan pemangkin pengoksidaan udara basah adalah lebih tinggi daripada proses lain seperti yang diramalkan. Kehadiran pemangkin mengurangkan keterukan keadaan operasi dan juga meningkat kadar penukaran.

CATALYTIC WET AIR OXIDATION OF WASTEWATER CONTAINING ACETIC ACID

ABSTRACT

Wastewater containing acetic acid has long been produced by the chemical industry. Improper disposal of the wastewater has become a major problem as it pollutes the environment and destroys aquatic ecosystem. The wastewater has to be treated before it can be released into the environment. Some of the treatment methods include membrane processes and wet air oxidation (WAO). These treatment methods have a few limitations. Membrane processes are limited by their solvent and thermal stability and WAO is only effective at severe operating conditions. In this research, catalytic wet air oxidation (CWAO) is the proposed method for treatment. The catalyst was synthesized according to the wetness method. The experiment was conducted by oxidizing simulated wastewater containing acetic acid in a batch reactor. The reaction study was repeated with the manipulation of two different operating parameters. The sample was analysed using Total Organic Content (TOC) analysis and Gas Chromatography (GC). The catalyst was characterized by X-ray diffraction (XRD) and Physisorption analysis (BET Method). CWAO yielded the highest conversion at the temperature of 80°C. The catalyst with high surface area was confirmed by XRD and BET. The conversion using CWAO was higher than other processes as predicted. The presence of the catalyst reduced the severity of the operating conditions and also increased the conversion rate.

CHAPTER 1

INTRODUCTION

1.1 Background of the Proposed Study

Industrial processes normally produce wastewater and this industrial wastewater is dangerous to be released into the environment. Some wastewater has higher concentration of certain chemicals while some are more dilute. Organic chemicals such as acetic acid are normally found in dilute industrial wastewater. There are many industries that produce wastewater containing acetic acid. Among these industries are the pharmaceutical industry, food and beverage industry (Kumar and Babu, 2008) and polymer manufacturing industry (Shin et al., 2009). Acetic acid is a weak acid and dilute wastewater containing acetic acid is harmful to the environment as it can contaminate and destroy the aquatic ecosystem. Therefore, industrial wastewater must be treated before being released into the environment. By removing the acetic acid from the wastewater, we can, on one hand make full use of our limited resources, and on the other, protect our environment (Yu et al., 2000).

Many methods have been utilized over the years to recover or remove acetic acid from the wastewater. Simple separation techniques such as liquid–liquid extraction, adsorption and distillation have proven to be ineffective (Kumar and Babu, 2008). More advanced methods such as membrane and oxidation methods are more widely used. One of the methods used to remove acetic acid is through wet air oxidation (WAO). WAO is an oxidation process that oxidizes dissolvable or suspended organic compounds as well as reducible inorganic compounds with oxygen or air under the circumstances of high temperature and high pressure in liquid phase. Catalytic wet air oxidation (CWAO) was a new technology developed on the basis of WAO in the 1970s (Zhu et al., 2002). The usage of catalyst can reduce the limitations of WAO by reducing the operating temperature, pressure and also reduce the reaction time.

Previous methods of treatment such as WAO proved ineffective as WAO has limited application due to the conditions of the process; high temperature, pressure and long reaction time (Mikulová et al., 2007). Membrane processes has limited solvent stability (Wee et al., 2008), thermal stability and are prone to fouling (Kumar and Babu, 2008). This indirectly increases the cost of the process. Hence, CWAO is a promising method and catalysts with high activity are needed to ensure higher conversion and a more effective way to remove acetic acid.

1.2 Research Objectives

The objectives of the present study are:

a) To synthesize and characterize the ruthenium oxide on zirconium oxide and cerium oxide support (RuO_2/ZrO_2-CeO_2) catalyst.

b) To examine the activity of the synthesized catalyst in the catalytic wet air oxidation of wastewater containing acetic acid.

1.3 Scope of the Study

The scopes of this study are the synthesis of RuO_2/ZrO_2-CeO_2 catalyst using the wetness method and determination of the activity of the synthesized catalyst in oxidizing the wastewater containing acetic acid. The important parameters include concentration of acetic acid in the wastewater, temperature and air flow rate. The analysis methods used to determine the acetic acid concentration are Total Organic Carbon (TOC) analysis and Gas Chromatography (GC). For the catalyst characterization, X–ray diffraction (XRD) and Physisorption analysis (BET Method) are conducted.

1.4 Significance of the Study

The significance of the proposed study is to synthesize the catalyst with high activity in oxidizing the wastewater containing acetic acid. The synthesized catalyst can be used in larger scale operations of treatment of wastewater containing acetic acid. Besides that, the treated wastewater can be safely released into the environment and prevent contamination and destruction of the aquatic ecosystem.

CHAPTER 2

LITERATURE REVIEW

This review discusses about industrial wastewater containing acetic acid, treatment methods and their limitations, catalytic wet air oxidation (CWAO) method and the type of catalyst used in CWAO.

2.1 Industrial Wastewater Containing Acetic Acid

A large number of chemical industries produce huge amounts of wastewater containing various amounts of toxic and hazardous organic compounds. A typical organic compound that is present in wastewater is carboxylic acid such as acrylic acid and acetic acid. Detailed analysis shows that acetic acid is the most commonly found organic acid with significant concentration. Acetic acid is not harmful to

humans if it is dilute, however, it is dangerous to the environment as it can contaminate and destroy the aquatic ecosystem.

There are many industries that produce wastewater containing acetic acid. Among these industries are the pharmaceutical industry, polymer manufacturing industry, food and beverage industry. In a research done by Kumar and Babu (2008), stated that acetic acid is most widely used in the field of food and beverages as an acidulant. They also said acetic acid is used in the synthesis of acetyl cellulose and plastics and also in the food industry, as well as in the printing and dyeing industries.

Slaughter house waste and animal by-products contains ammonia and organic residue which include acetic acid. Animal by-products and slaughter house waste are produced daily and must be dealt with to prevent pollution. The acetic acid in in animal by-products can be treated by means of CWAO, as researched by Frontanier et al. in 2010. Another source of acetic acid waste comes from the silicon wafer manufacturing. The acetic acid is in the wafer etching process. Due to a rapid growth of those industries in Korea, the amount of waste acids generated during etching and cleaning processes is increasing rapidly (Shin et al., 2009).

2.2 Treatment Methods

Before wastewater can be released into the environment, it has to be treated until it meets a standard set by the Department of Environment. Many methods have been utilized over the years to recover or remove acetic acid from the wastewater.

Simple separation techniques such as adsorption and distillation have proven to be ineffective. More advanced methods such as membrane and oxidation methods are more widely used.

2.2.1 Adsorption and Distillation

Adsorption and distillation are well known separation methods. These methods are more focused on removing the acetic acid from the water. Adsorption is another good method to remove acetic acid but the cost associated with regeneration of commercial adsorbents makes adsorption operation very expensive (Kumar and Babu, 2008). Distillation has a disadvantage as it is only effective when the concentration of acetic acid in the wastewater is high (Helsel, 1977).

2.2.2 Membrane Processes

Membrane process is an effective method to recover or remove organic contaminants from wastewater. Basically, membrane process is a form of filtration where wastewater goes through a membrane and the contaminants remain and cleaner water is produced. Ultra filtration, reverse osmosis and pervaporation are some the of membrane processes. The choice of the membrane is a key consideration that defines the type of application (Jullok et al., 2011). Normally, the smallest weight fraction of component in the mixture is to be transported across the

membrane: hydrophilic polymeric membranes are used for the dehydration of organic liquids and hydrophobic polymeric membranes for removal of organics from water streams (Kujawski, 2000). However, polymeric membranes have limitations. Polymeric membrane has limited solvent stability (Wee et al., 2008) and thermal stability. Besides that, another problem with membrane process is the membrane fouling which requires frequent cleaning (Kumar and Babu, 2008).

2.2.3 Wet Air Oxidation

Wet air oxidation (WAO) is defined as the liquid phase oxidation of organic compounds at temperatures (125–320°C) and pressures (0.5–20MPa) below the critical point of water using a gaseous source of oxygen (Mishra et al., 1995). WAO process is also defined as a thermochemical process where several active oxygen species, including hydroxyl radicals, are formed at elevated temperatures (i.e. 200–300°C) and pressures (i.e. 2–20MPa) (Katsoni et al., 2008).

This method works on the principles where low molecular weight pollutant molecules such as acetic acid to carbon dioxide and water if the conditions are severe enough. As a general rule, the oxidation rate increases with an increase in molecular weight of the organic acid (Klinghoffer et al., 1998). Although this method is a well-established technique, it has certain limitations. Severe operating conditions, low oxidation rate of low molecular weight compounds and increased equipment and operating costs (Verenich et al., 2000) are some of the limitations.

Several researches using WAO was conducted and investigated. WAO of long-chain carboxylic acids such as caprylic and oleic acids was determine to be effective where conversions of 90% and greater were achieved in 10 minutes (Sánchez-Oneto et al., 2004). As stated previously, to achieve high conversion or oxidation, operating conditions must be severe (Duprez et al., 2003 and Yang et al., 2010).

2.2.4 Catalytic Wet Air Oxidation

Catalytic wet air oxidation (CWAO) is an improvement over the WAO method with the introduction of a catalyst in the reaction. Introduction of a catalyst into the reaction not only reduces the severity of the operating conditions such as temperature (Wang et al., 2008), but also increases the oxidation rate. Homogeneous and heterogeneous can be used in the reaction, but heterogeneous catalyst are preferred because no catalyst recovery step is required (Klinghoffer et al., 1998). This method overcomes the limitations of membrane and WAO techniques.

Many researches compared the efficiency of WAO and CWAO and how the introduction of catalysts improves the oxidation process. Duprez et al. (2003) concluded that CWAO processes, with homogeneous or heterogeneous catalysts, require milder reaction conditions. Yang et al. (2010) investigated the efficiency of WAO and CWAO in oxidizing of complex and high-loaded industrial wastewater and concluded that CWAO is highly efficient for wastewater treatment.

2.3 Catalyst for Wet Air Oxidation

The usage of catalyst in reactions has long been established in the chemical industry. Catalyst can either promote or inhibit a certain reaction. Catalysts that promotes a reaction is called a *promoter* while catalysts that inhibits a reaction is called an *inhibitor*. There are two types of catalyst, homogeneous catalyst and heterogeneous catalyst. Homogeneous catalysts are catalysts that are in the same phase as the reactants while heterogeneous catalysts are of different phase than the reactants (Fogler, 2006). In catalytic wet air oxidation, the type of catalyst used is heterogeneous catalyst. Heterogeneous catalysts are normally solids and are made from metals. Suitable metals that used in the catalyst ranges from metal oxides (Font et al., 1999 and Hung, 2009), transition metals (Gomes et al., 2005) and noble metals (Barbier Jr. et al., 2010 and Wang et al., 2008).

2.3.1 Metal Oxides and Transition Metals

Metal oxides and transition metals have been used as catalyst in catalytic wet air oxidation. The heterogeneous catalyst that have been used are Cu, Pd, CoO/ZnO, Cu:Mn:La oxides on spinal supports (ZnO, Al_2O_3), copper chromite, iron oxide, Co:Bi complex oxides and Mn/Ce (Klinghoffer et. al., 1998, Gomes et al., 2005, Hung, 2009, Arena et al., 2012). Despite having established the effectiveness of these metals as catalyst, they have also been proven to have some flaws. In a research done by Mikulová et al. (2007), partial leaching of metal ions has been

observed during the reaction, and a recovery step is necessary. This additional recovery step will increase the cost of wastewater treatment and this is undesirable.

2.3.2 Noble Metals

Noble metals are a class of metals that are highly resistant to corrosion and oxidation. Supported noble metals (including Pt, Pd, Ru, and Rh) have been proposed for the CWAO (Mikulová et al., 2007, Barbier Jr. et al., 2010, Wang et al., 2008). Activity wise, Imamura et al. (1988) studied the catalytic effect of noble metals on the wet oxidation of phenols and other model pollutant compounds, and found that ruthenium, platinum and rhodium were more active than homogeneous copper catalyst.

2.3.3 Potential Applications of RuO_2/ZrO_2-CeO_2 Catalyst

This section reviews the potential application of the RuO_2/ZrO_2-CeO_2 catalyst in other reaction systems. As this catalyst is used for CWAO of acetic acid wastewater, this review will give a better insight the potential of this catalyst for the CWAO of other types of wastewater.

2.3.3.1 CWAO of Phenolic Compounds

For the treatment of wastewater containing phenolic compounds such as phenol, noble metal catalyst has been proven to work effectively to remove phenol. Research done by Pintar et al. in 2008 shows that Ru/TiO_2 catalyst not only enables complete removal of phenol, but also removed total organic carbon (TOC) without the formation of carbonaceous deposits. Barbier et al. (2005) also demonstrated the activity order of CeO_2 supported noble metals for the CWAO of phenol as follows:

$$Ru/CeO_2 > Pd/CeO_2 > Pt/CeO_2$$

The introduction of ZrO_2 into the CeO_2 increases the mechanical strength, specific surface area and adsorption capacity of the catalyst. When used in CWAO of phenol, phenol and TOC removal stabilized approximately 100% and 96% respectively (Wang et al., 2008). This shows that the RuO_2/ZrO_2-CeO_2 catalyst can be applied to CWAO of phenolic compounds.

2.3.3.2 CWAO of N-Containing Compounds

Nitrogen-containing compounds are normally present in organic waste and are highly toxic as they can cause acidification of the ecosystem. Some nitrogen-containing compounds such as ammonia and aniline can be treated using CWAO. Aniline is a representative compound of N-containing aromatic compounds and is mainly used as a chemical intermediate in the production of polymers, pesticides, pharmaceuticals, and dyes (Ersöz and Atalay, 2010).

Many researchers have utilized ruthenium catalyst in the CWAO of aniline. Barbier et al. (2005) used a Ru/CeO_2 catalyst while Reddy and Mahajani (2005) used a Ru/SiO_2 catalyst in the CWAO of aniline. As ruthenium is applicable as a catalyst for the conversion of aniline, RuO_2/ZrO_2-CeO_2 has great potential in the reaction of aniline as it may improve on the current reaction rate and conditions.

Ammonia is widely used as a chemical in the manufacture of ammonium nitrate, metallurgy, petroleum refineries, etc. It is known as a key intermediate in the oxidation of N-containing compounds and is not amenable to direct biological treatment due to its toxicity (Ihm and Kim, 2011). Barbier et al. (2002) showed that CWAO is a very effective way to removal of ammonia where ammonia is converted in to elemental nitrogen.

Other research also used ruthenium as a catalyst in the oxidation of ammonia. Ru/TiO_2 was used to remove ammonia (Lee et al., 2005) and it was concluded in that research that ruthenium catalyst was responsible for the oxidation of ammonia and does not affect the selectivity of the formation of nitrogen. RuO_2/ZrO_2-CeO_2 catalyst can be researched to see whether it can oxidize ammonia.

In this research, the researcher is using a ruthenium oxide on zirconium oxide and cerium oxide support (RuO_2/ZrO_2-CeO_2) catalyst. The selection of ruthenium as the catalyst is based on its resistance towards sintering by carbonaceous species during CWAO. Therefore, compared to the platinum catalysts, the equivalent ruthenium materials demonstrate higher resistance against poisoning by carbonaceous species during the CWAO experiments (Gaálová et al., 2010). Ruthenium catalyst has more significant activity compared to platinum catalyst and this is proven in a research done by Perkas et al. (2005).

Table 2.1 Catalyst Type and Their Advantages and Disadvantages.

Catalyst Type	Advantage	Disadvantage
Metal Oxides and Transition Metals	Cost of catalyst is cheaper compared to noble metal catalyst	Partial leaching of metal ion and recovery step is needed (Mikulová et al., 2007)
Noble Metals	High activity (Imamura et al., 1988) , resistant to poisoning by carbonaceous species (Gaálová et al., 2010)	Noble metal catalyst is more expensive than metal oxides and transition metal catalysts

2.4 Catalyst Synthesis Methods

There are many methods to synthesize catalyst and many researchers utilize different methods to synthesize their own type of catalyst, specific to their research. The choice of synthesis methods depends on the final catalyst desired, especially its physical and chemical composition. Generally, the methods may contain the same procedure, but the overall method is unique by itself. In a research conducted by Perego and Villa in 1997, they discussed on the catalyst preparation method. Their paper included on the different methods used to prepare catalysts which are bulk catalyst and support preparation and impregnation method, which will be reviewed in the following subtopics.

2.4.1 Bulk Catalyst and Support Preparation

Bulk catalysts are actually the active substance or the active precursors of the catalyst. Examples of bulk catalyst include silica-alumina for hydrocarbon cracking, Zn-Cr oxide for the conversion of CO-H_2 mixtures to methanol and iron-molybdate for methanol oxidation (Perego and Villa, 1997). Bulk catalysts are further divided into two different types of preparation which are precipitation and sol-gel method. Both these methods have similar steps, but the precipitate that forms separates these two methods.

2.4.1.1 Precipitation Method

Bulk catalyst synthesized using the precipitation method is a simple synthesis method where the active substance is precipitated from a liquid solution and is the base for the catalyst itself. Generally, the precipitate contains the active substance and will slowly become the final, desired catalyst as it progresses.